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SATELLITE BANDS NEAR HIGH MEMBERS OF THE CESIUM ABSORPTION SPECTRUM

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One of the spectral effects which as yet is not well understood is the appearance of diffuse satellite bands near atomic lines in the spectra of gaseous mixtures. Two different types of satellite bands have been reported in the past:<sup>1</sup> (1) bands appearing on the short wavelength side of the atomic lines ("Violet Bands") and (2) bands appearing on the long wavelength side of the atomic lines ("Red Bands"). Slide 1 gives an example of the "violet" bands. The picture on the left shows the  $2p_{1/2}$  component of the Cs resonance lines as it appears in the absorption spectrum of pure Cs vapor. The picture on the right shows the same line as it appears in the absorption spectrum of the gaseous mixture of Cs and Xe.

The line is broadened and is accompanied by a violet satellite band. Slide 2 gives an example of the "red" bands. The two pictures on this slide are the second and third doublets of Cs as they appear in the spectrum of the Cs-Xe mixture. Each line in these pictures is accompanied by a "red" satellite band.

An important aspect of the study of the satellite bands is that this study promises to supply detailed information on the nature and properties of forces acting between free atoms and molecules in gaseous mixtures. Especially interesting in this respect is the fact that the bands are indicative not only of the forces acting between atoms and molecules in their ground states, but also of the forces acting between excited atoms and molecules.

Although no generally accepted and complete theory of the satellite bands is presently available, it is clear that the positions of the bands

reflect the perturbation of the term level diagram of the radiating atom caused by the presence of a foreign gas atom in the neighborhood of the radiating atom. One, therefore, customarily describes the bands by means of a term level diagram drawn as a function of the internuclear separation between the atoms. On such a diagram, each term constitutes a potential curve representing the interaction energy of the two atoms.

Slide 3 shows how the satellite bands can be explained by means of such a diagram. The drawing on the right depicts several term levels of an isolated Cs atom. A transition from the ground state level to an excited state level results in an unperturbed Cs line of frequency  $\nu_0$ . In the drawing on the left, the ground state level and the first excited state level of Cs are represented as a function of the separation between the Cs atom and a foreign gas atom. The two levels are represented by curves of different shapes, and hence the transitions occurring at different internuclear separations correspond to frequencies, the superposition of which on a photographic plate forms the structure shown in the lower drawing on the left side of the figure. The intensity distribution in this structure is governed primarily by the probability of occurrence of different internuclear separations. This probability is represented by the upper left hand drawing. As it follows from the three drawings on the left, one does, indeed, expect to see a "red" satellite band of frequency  $\nu_1$  and a violet satellite band of frequency  $\nu_2$  near the Cs line  $\nu_0$  provided of course the potential curves shown are substantially correct. The "violet" band corresponds to transitions at close internuclear separations (repulsive part of the potential curves) while the "red" band corresponds to transitions at larger separations.

It must be pointed out that the above interpretation of the bands which originated with Freston<sup>2</sup> has recently been criticized by Klein and Margenau<sup>3</sup> who favor a somewhat different mechanism. However, inasmuch as they too attribute the violet bands to transitions taking place at close internuclear separations, the discussion that follows is equally applicable to their mechanism as well. Following these introductory remarks, we shall now report some new experimental data on the satellite bands and shall discuss some of the consequences of these data.

In studying the spectra of Cs - hydrocarbon mixtures, we have observed a series of "violet" bands that have not been reported previously. These bands possess three characteristics which make them difficult from any bands already reported. These characteristics are: (1) the fact that the bands are present only at the fourth and higher doublets of the Cs absorption series, (2) the fact that the bands apparently experience a shift identical with the shift of the parent lines, and (3) the fact that the band-line separations for these bands decrease with increasing order of the doublets with a remarkable regularity.

Slide 4 shows these bands as they appear in the mixture of Cs - neohexane. The picture shows the 6th - 13th doublets of Cs with their associated bands. Slide 5 shows the dependence of the band-line separation on the ordinal number of the Cs doublets. As one can see, the separation is a smoothly varying function of the ordinal number and approaches "zero" for high doublets.

There are three reasons why we find these bands especially interesting. The first reason is that the bands exhibit a shift just as the lines do. Since the shift is a result of multiple collisions between the radiating atom and the foreign gas atoms, this property of the bands forms a simple proof that the bands as such must be a result of single collisions. The second reason is that the steady decrease of the band-line separation with the ordinal number of the doublet is irreconcilable with the usual supposition that the "violet" bands are due to transitions at very close internuclear distances. Indeed, the fact that the band-like separations approach zero for very high members must mean that either the excited state curves for large principal quantum numbers become identical with the ground state curve, or that the bands are due to transitions originating from the flat part of the ground state potential curve. Since the excited state curve cannot be identical with the ground state curve for obvious reasons, we are forced to conclude that the bands are due to transitions originating on the flat part of the ground state curve.

The third reason that we regard the bands to be of special interest is that they are observed only for the high members of the series. This, we believe, indicates that the bands are a result not of Van der Waal's interaction between particles, but rather a result of "internal" perturbation of the excited atom by a foreign particle located well within the electron cloud of the valence electron of the radiating atom. Slide 6 illustrates this effect. In the ground state, the radiating and the

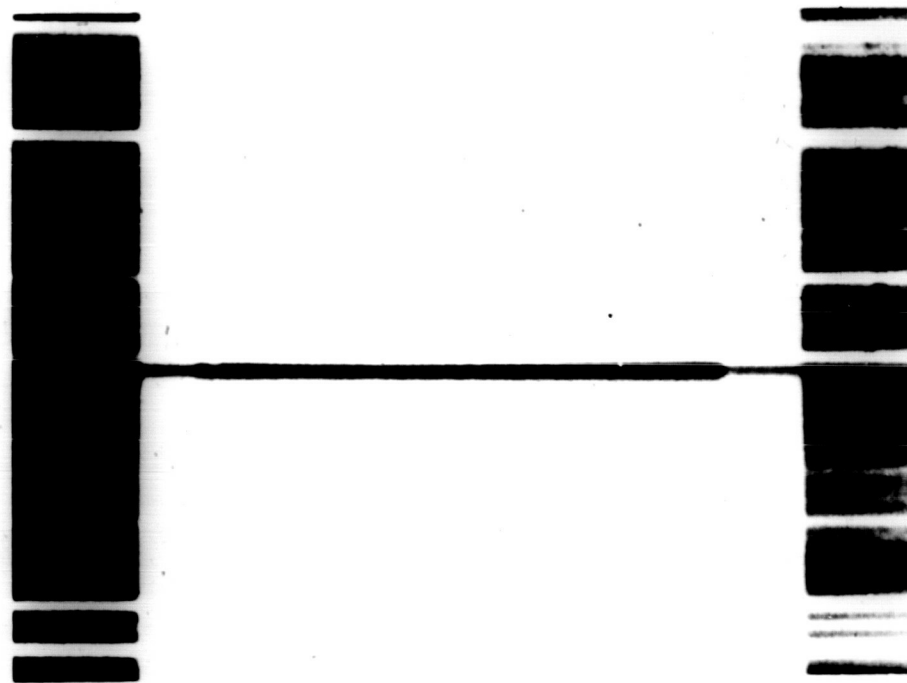
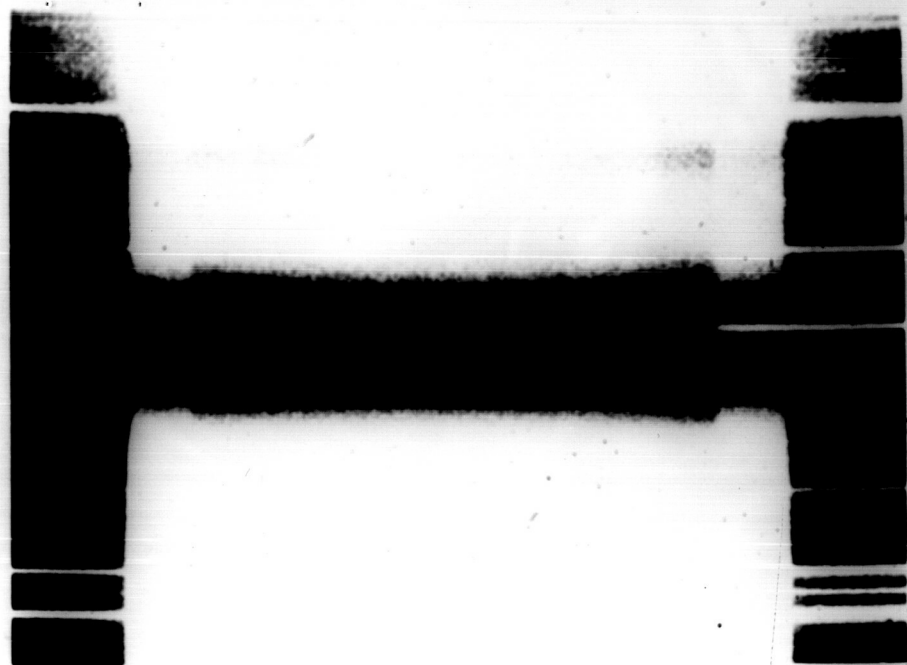
foreign gas atoms are completely outside each other and there is essentially no interaction between them. However, when the radiating atom undergoes a transition to a highly excited state, the foreign gas atom becomes trapped within the valence electron shell and causes a perturbation of the energy levels of the radiating atom. There are several effects which could be responsible for such perturbations. For instance, the creation of an axial electric field resulting from the polarization of the foreign gas atom by the atomic core of the radiating atom; also the change of the penetrability of the atomic core by the valence electron; and the attraction of the foreign gas atom by the atomic core. Whether or not these effects can account for the new bands is not quite clear and will have to be determined by a separate investigation.

The existence of these bands makes it clear, however, that a thorough analysis of these internal perturbation effects should be made before a complete and coherent theory of the satellite bands could be devised.

# REFERENCES

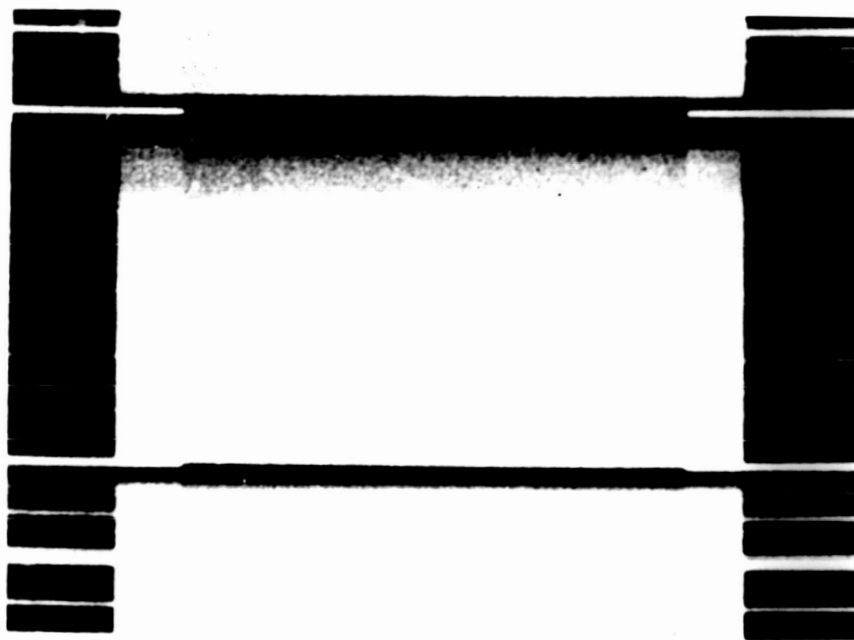
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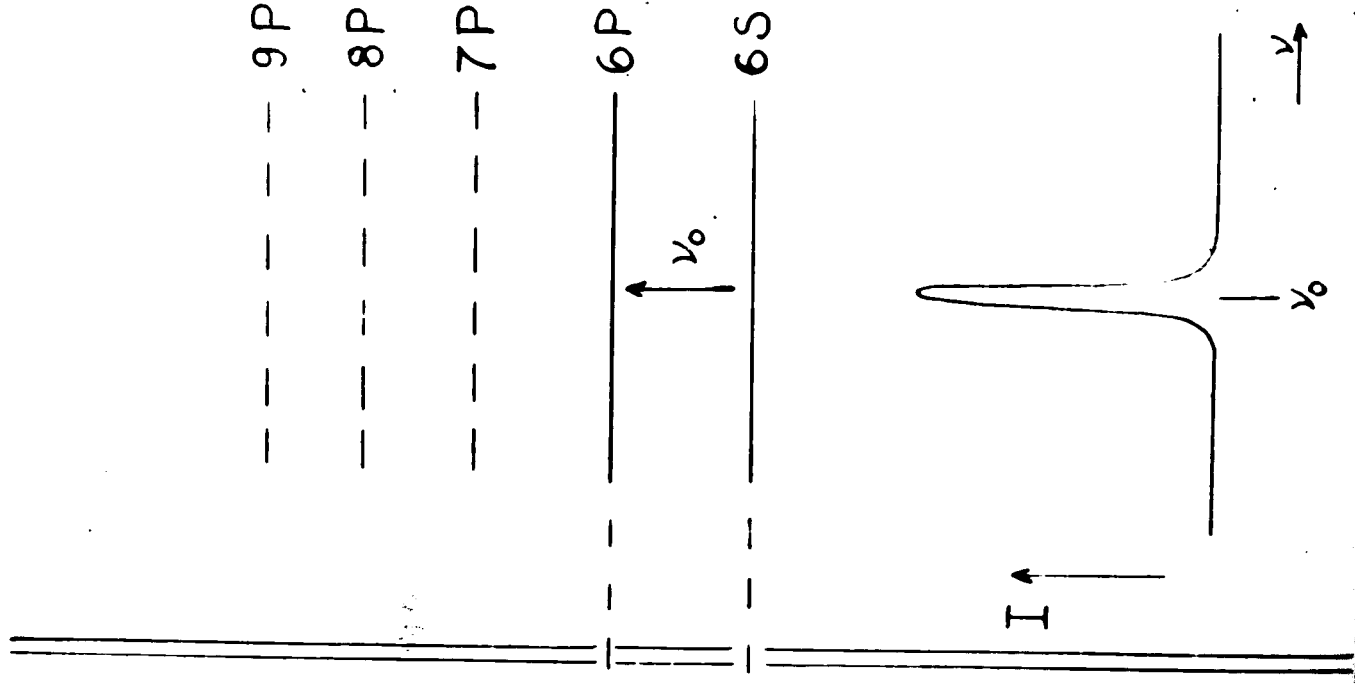
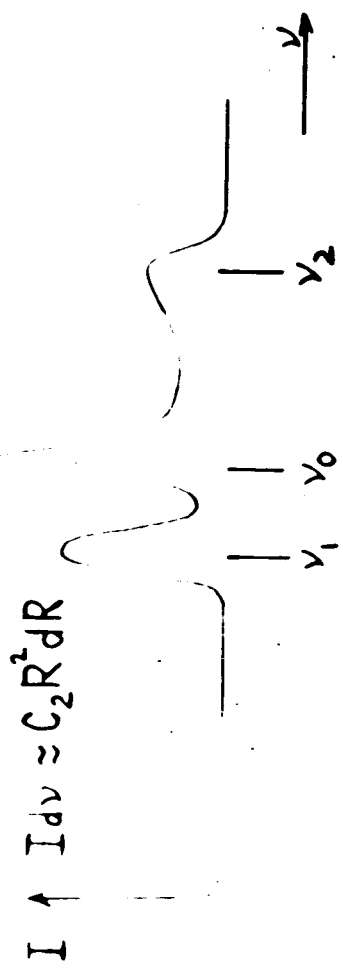
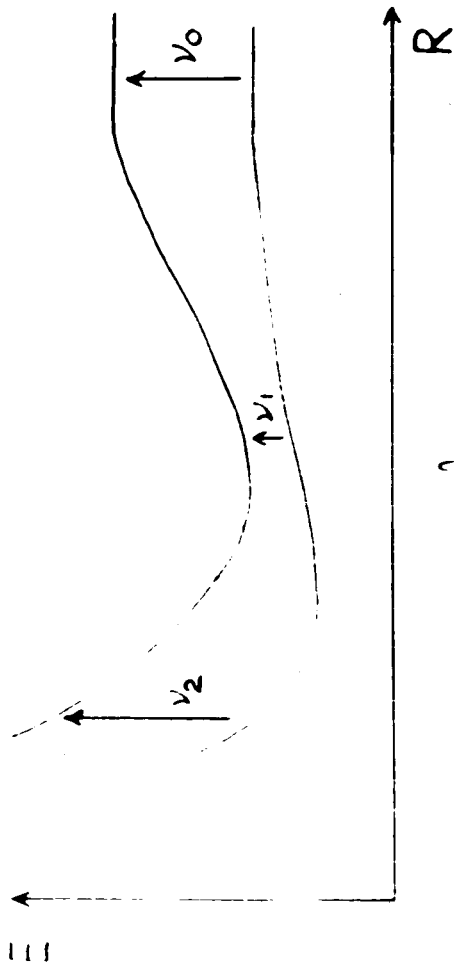
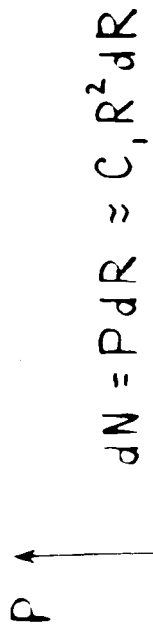




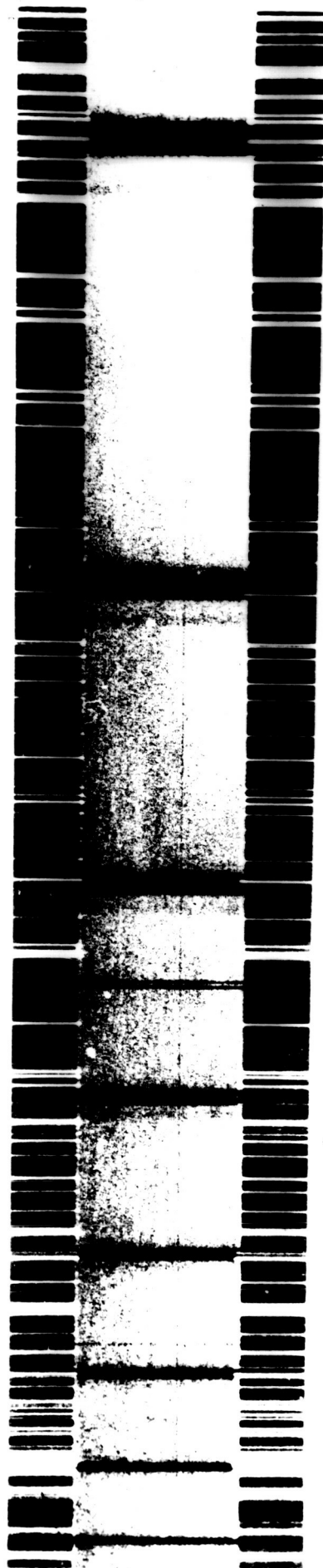
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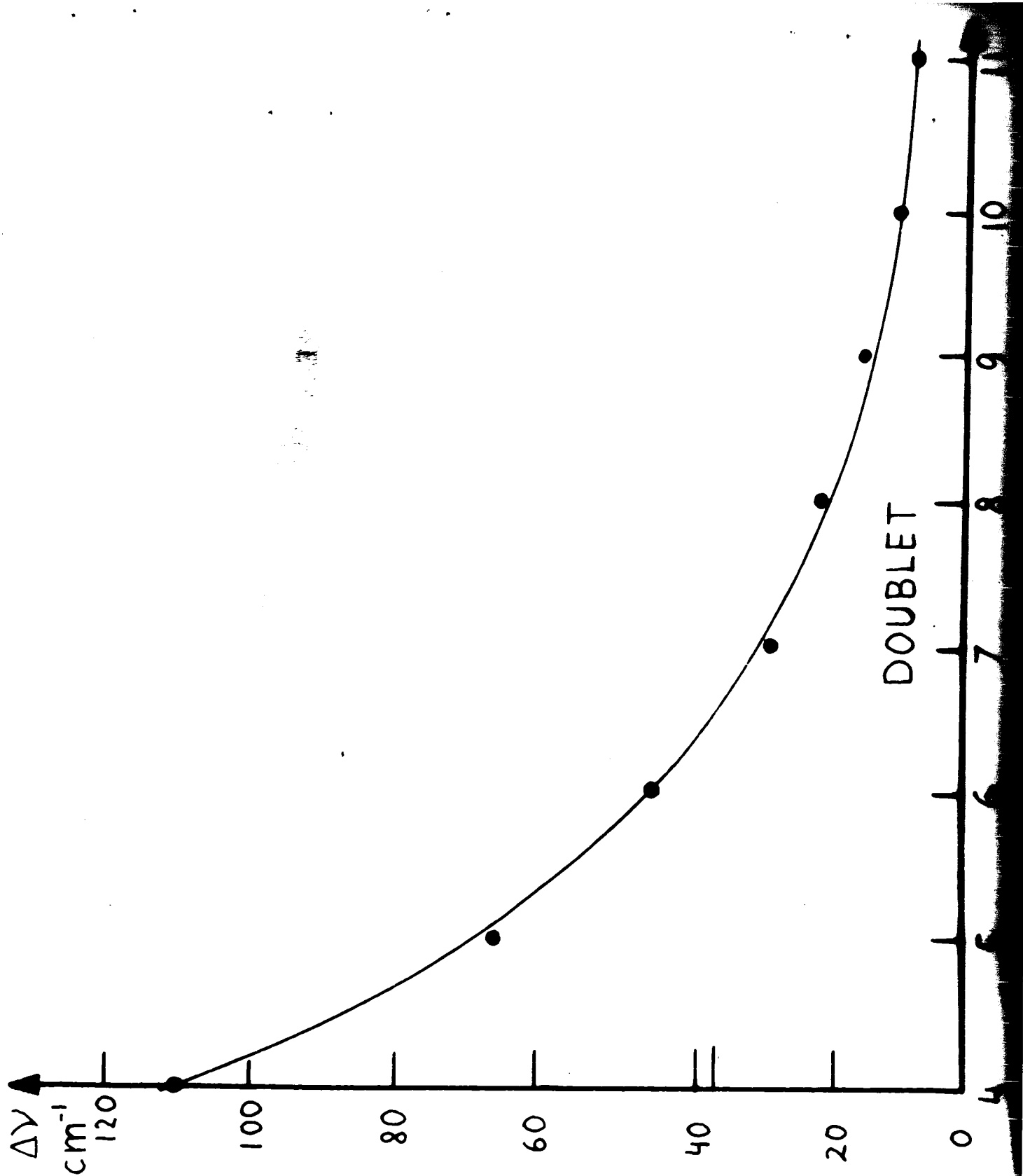
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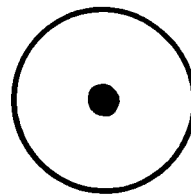
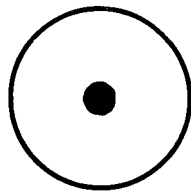
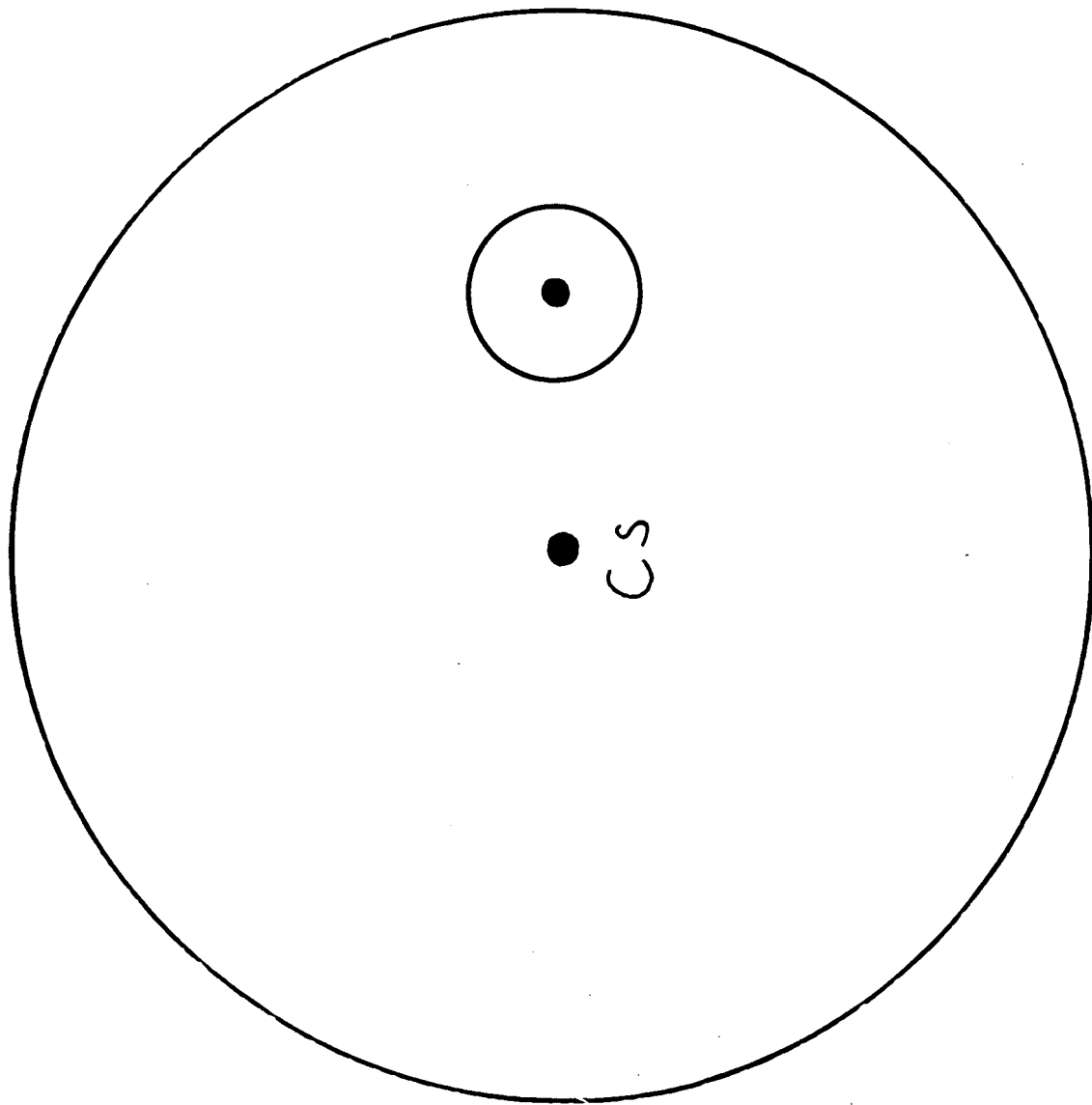
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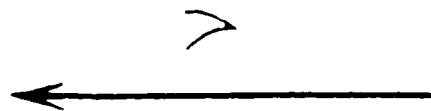
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